

COMPARATIVE ELEMENTAL ASSOCIATIONS IN LIGNITES
HAVING SIGNIFICANT WITHIN-MINE VARIABILITY OF SODIUM CONTENT

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Introduction

The inorganic constituents of lignites from the Fort Union Region are distributed within the coal matrix as cations, coordinated species and minerals (1). The quantities of inorganics present in these lignites have significant within-mine, or intramine, variability (2). Studies have indicated that high-sodium coals from this region cause severe ash fouling of heat exchange surfaces in utility boilers (3). The coals investigated were collected from pits within the Gascoyne Mine, Bowman County, North Dakota and Beulah Mine, Mercer County, North Dakota. From each mine, two samples were selected having significant differences in sodium content and different fouling characteristics in utility boilers.

The distribution of inorganics constituents within the Gascoyne and Beulah coals was determined by non-quantitative identification of mineral matter and by chemical fractionation to ascertain any significant differences in the association of elements within the coals. In addition, the amounts of ion exchangeable cations were related to the carboxylate content of the coals.

Experimental

Samples were collected according to a procedure used by Benson (4). Proximate and ultimate analyses were performed on the air-dried coals using standard ASTM methods (5). Bulk coal mineralogy was determined by x-ray diffraction (XRD) of the coal's low-temperature ash (LTA) (6) and by scanning electron microprobe (SEM) in conjunction with energy dispersive x-ray analysis (EDX) (7) of the coal. Carboxylate contents were determined by exchanging the demineralized coals (8) with 1M barium acetate, followed by potentiometric titration with 0.2N barium hydroxide to pH 8.25 to determine the acid produced (9). The determination of inorganic constituents of the starting coals and subsequent residues was performed by x-ray fluorescence (XRF) (10) and neutron activation analysis (NAA) (11). The chemical fractionation was done with a method modified from that of Miller and Given (1). Two samples of each coal were ground to less than approximately 325 mesh in an alumina grinder and freeze dried for two days. The dried coal was mixed with 100 ml of 1N ammonium acetate and stirred for 24 hours at 70°C in a plastic beaker. The mixture was filtered, the residue washed, and the extract made up to 250 ml. The dried residue was extracted two more times with ammonium acetate, then twice with 1N hydrochloric acid in the same manner. All of the extracts were analyzed with inductively coupled argon plasma spectrometry (ICAP). A portion of the residue left after the ammonium acetate extractions and a portion left after the hydrochloric acid extractions were analyzed by XRF and NAA.

Results and Discussion

Coal Compositions. Table I shows the initial elemental, proximate, ultimate, and carboxylate content analysis of the coals on a moisture free basis.

Table I. Dry Bulk Coal Elemental, Ultimate, Proximate, and Carboxylate Analyses

	Gascoyne Low Sodium	Gascoyne High Sodium	Beulah Low Sodium	Beulah High Sodium
Na ($\mu\text{g/g}$)	1317	2694	1379	4625
Mg ($\mu\text{g/g}$)	2991	2588	1476	979
Al ($\mu\text{g/g}$)	8740	7300	5420	2890
Si ($\mu\text{g/g}$)	28640	10920	8950	3530
K ($\mu\text{g/g}$)	1260	1430	916	ND*
Ca ($\mu\text{g/g}$)	17370	22790	15610	18110
Ti ($\mu\text{g/g}$)	1180	546	503	583
Mn ($\mu\text{g/g}$)	123	163	52	24
Fe ($\mu\text{g/g}$)	3890	2540	10240	5160
Ba ($\mu\text{g/g}$)	593	1268	179	397
C (wt %)	58.3	54.5	61.4	66.4
H (wt %)	4.0	5.2	4.1	3.6
N (wt %)	0.88	0.84	0.42	0.87
S (wt %)	1.7	1.4	3.2	1.2
O (diff.)	19.6	29.3	18.2	19.5
Ash (wt %)	15.5	8.8	12.6	8.4
Carboxylate groups (meq/g)	2.46	2.54	2.47	2.76

*ND - Not determined.

Similarities can be seen between the high-sodium coals versus their intramine low-sodium counterparts. In the high-sodium coals, the carboxylate, calcium, and barium contents are greater. Magnesium, aluminum, silicon, iron, and ash contents are lower in the high-sodium coals than in their intramine low-sodium counterparts.

Coal Mineralogy. The mineralogies of the coals, determined by x-ray diffraction of their low-temperature ashes, are similar. The diffractogram shown in Figure 1 is of the LTA of the Gascoyne high sodium coal. The mineral phases which were in sufficient amounts (2-5% depending on crystal structure) to be clearly delineated include quartz (SiO_2), micaceous clay minerals, and pyrite (FeS_2). Some bassanite ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) was identified in the LTA of the Beulah coals although it is not clear if this forms from sulfur fixation during ashing (12) or from the dehydration of gypsum. The quartz peaks are more prominent in the diffractograms of the ash from the low-sodium (high-ash) coals.

In addition to the minerals mentioned above, the SEM-EDX work showed minor amounts of dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), gypsum

($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), rutile (TiO_2), hematite (Fe_2O_3) (7), and barite (BaSO_4) (7). Also, the micaceous clay minerals identified by XRD were seen to include kaolinite, illites, and micas. Most of the SEM-EDX work was not systematic so quantitative comparisons between the coals will not be made here.

Ammonium Acetate Treatments. The percentages of the elements removed from the coals by the ammonium acetate treatments are shown in Table II. The figures for the carboxylate ions are percentages of the carboxyl groups that are in a salt form, under the assumption that all of the cations removed by the ammonium acetate treatments were exchanged from these sites. Minor amounts of these elements may have been exchanged from other organic acids or micaceous clays, or may have come from the dissolution of minerals soluble in ammonium acetate such as gypsum, calcite, and dolomite.

Table II. Elements Removed by Ammonium Acetate (%)

	Gascoyne Low Sodium	Gascoyne High Sodium	Beulah Low Sodium	Beulah High Sodium
Na	100	100	100	100
Mg	74	75	76	84
Al	0	0	0	0
Si	0	1	0	0
K	22	19	7	*31
Ca	78	85	82	77
Ti	0	0	0	0
Mn	34	39	25	21
Fe	0	0	0	0
Ba	39	61	72	88
Carboxyl groups (% in salt form)	38	51	32	35
*ppm removed				

The results indicate aluminum, silicon, titanium, and iron are not removed from any of the coals by this treatment. Among those elements that are extracted, a higher percentage of barium is removed from the high-sodium coals than from their intramine low-sodium counterparts. However, more barium is removed by each of the second and third treatments than by the first so we feel that the barium extraction was incomplete. A large percentage of the sodium, calcium, and magnesium was removed from all of the coals.

Hydrochloric Acid Treatments. Table III lists the percentage of elements removed by the hydrochloric acid treatments. The elements removed by this treatment were associated with the coal as oxides, carbonates, coordinated complexes within the coal organic structure and certain elements (Mg, Al, Si, K, Ca, Fe) which can be extracted from the micaceous clay minerals.

A higher percentage of aluminum was removed from the high-sodium (low-ash) coals than from the corresponding intramine low-sodium

Table III. Elements Removed by Hydrochloric Acid (%)

	Gascoyne Low Sodium	Gascoyne High Sodium	Beulah Low Sodium	Beulah High Sodium
Na	0	0	0	0
Mg	12	16	17	16
Al	42	51	60	80
Si	3	12	14	12
K	30	41	19	*206
Ca	20	14	17	22
Ti	4	7	5	2
Mn	64	60	69	76
Fe	73	68	37	42
Ba	43	39	16	12

*ppm removed

(high-ash) coals. Although more aluminum was actually removed from the low-sodium coals, we feel that the solutions were not saturated because much lower levels of aluminum were found in the second extracts than in the first. Instead, we believe that the higher relative removal from the high-sodium coals is due to differences in the types of micaceous clay minerals present. In all the coals the ratio of aluminum to silicon removed (4:1 - 14:1) does not match the ratios found in common micaceous clay minerals. This indicates that the micaceous clays have not dissolved but that a selective attack has occurred on the gibbsite (aluminum containing) layer in the micaceous clays.

Insolubles. Table IV shows the elemental percentages left in the residue after the chemical fractionation process.

Little or no sodium, magnesium, calcium, and manganese remain in the coals. X-ray diffraction of the low temperature ash of the residue from the Gascoyne high-sodium coal shows that the major remaining minerals are the same as those seen in the LTA of the bulk coal; i.e., quartz (SiO_2), micaceous clays, and pyrite (FeS_2). Work done with the SEM-EDX suggests that the potassium remaining in the residue is found in the micaceous clays, titanium in a rutile form (TiO_2), and the barium present as barite (BaSO_4)(7). It is interesting that no barium is left in the high-sodium coals even though they originally contained more barium than the low-sodium coals.

Conclusions

The amount and mode of occurrence of inorganics in lignites can have a pronounced effect on the efficiency of the coal's utilization. This study used a number of the techniques developed by others to investigate variations in the inorganic makeup of coals found in two areas within each of two mines. By better understanding these

Table IV. Elements Remaining After All Treatments (%)

	Gascoyne Low Sodium	Gascoyne High Sodium	Beulah Low Sodium	Beulah High Sodium
Na	0	0	0	0
Mg	14	9	7	0
Al	58	49	40	20
Si	97	87	86	88
K	48	40	74	*ND
Ca	2	1	1	1
Ti	96	93	95	98
Mn	2	1	6	3
Fe	27	32	63	58
Ba	18	0	12	0

*Not determined.

variations, insights into the various depositional and post depositional processes may be gained. Also, understanding the modes of occurrence of the inorganic constituents of a coal may help in determining its appropriate utilization.

A comparison of the elemental associations between the high-sodium coals and their intramine low-sodium counterparts shows:

1. No significant differences in the modes of occurrence of the inorganic constituents exist, only differences in the amounts of inorganic species.
2. A higher percentage of aluminum is extracted from the high-sodium coals indicating different types of predominant micaceous clay minerals.
3. A higher percentage of barium is associated with ion exchange sites in the high-sodium coals.

Further work needs to be done in determining the exact mineralogic makeup and types of organic acids found in the coals, as well as accumulating more data from which to draw further conclusions.

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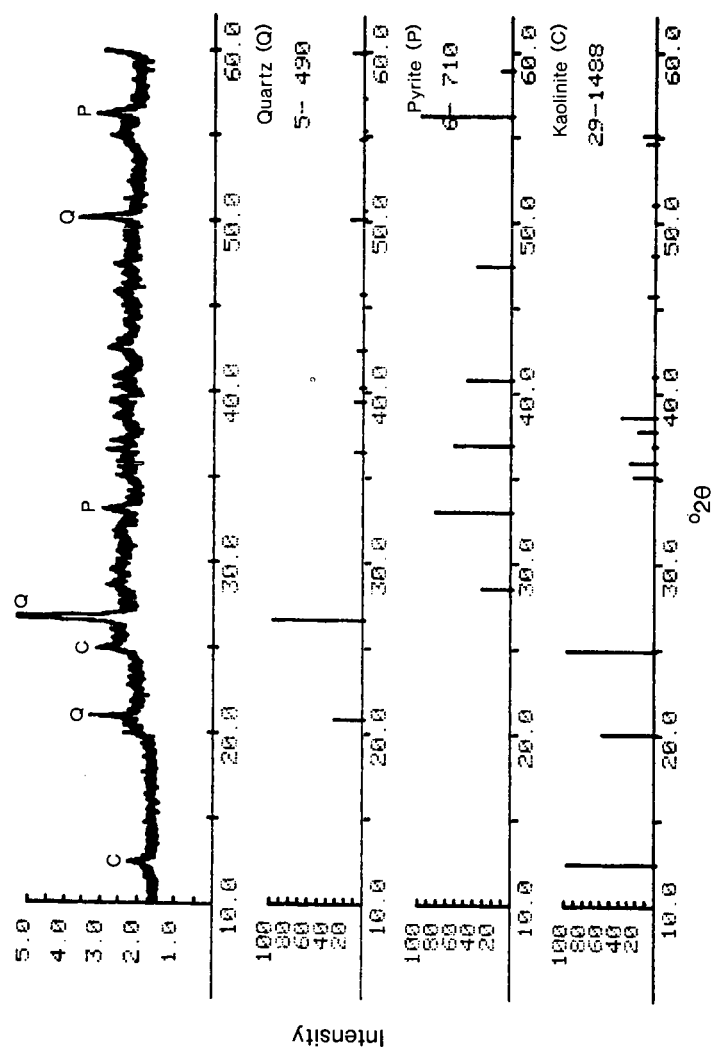


FIGURE 1. Diffractogram of the Gascoyne High-Sodium LTA along with reference graphs for quartz, pyrite, and kaolinite.